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Intensity of two-photon absorption transitions for Ni^{2+} in MgO

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Abstract

The parity-allowed two-photon transitions between the ground state $^3A_2(T_2)$ of the configuration $3d^8$ in cubical symmetry and the excited states of the same configuration are obtained via a simple model. This model is developed in a symmetry adapted framework by using second-order mechanisms and ionic wave-functions. It is applied to the recent experimental results obtained by McClure and co-workers for Ni^{2+} in MgO.

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I. INTRODUCTION

In recent years, two-photon absorption spectroscopy of partly-filled shell (rare-earth and transition-metal) ions in solids have received a great deal of attention. Major achievements have been done both from an experimental and theoretical viewpoint (see, for instance, Refs. 1-13). The main theoretical developments concern : (i) the use, in addition to the Axe second-order mechanism, of higher order mechanisms describing spin-orbit, crystal-field, ligand polarizibility, and electron correlation effects and (ii) the application of symmetry adaptation techniques. More specifically, it has been shown recently how quantitative, rather than only qualitative,[2] symmetry considerations can be used to obtain the polarization dependence of a two-photon absorption between two Stark (rather than $[^{2S+1}L]_J$) levels.[8,9,11]

Recently, results on two-photon spectroscopy of Ni^{2+} in MgO have been reported by Moncorgé and Benyattou[12] and by McClure and co-workers.[13] It is then the aim of the present paper to further contribute to test theoretical models for analysing two-photon spectroscopy by using the fresh data of Ref. 13.

We shall develop, in Secs. II and III, a simple quantitative model for dealing with the d^8 (or d^2) configuration in octahedral symmetry. The results provided by this model for MgO:Ni^{2+} are given in Sec. IV and discussed in Sec. V.

II. THEORY

The transition matrix element $M_{i\rightarrow f}$ for a two-photon absorption between an initial state i and a final state f is given by the Göppert-Mayer formula

$$M_{i\rightarrow f} \;=\; \sum_{v} \frac{(f|\vec{D}.\vec{\mathcal{E}}|v)\;(v|\vec{D}.\vec{\mathcal{E}}|i)}{\hbar\omega - E_v}\;, \tag{1}$$

where the sum on v extends over all intermediate states. In Eq. (1), E_v denotes the

energy of the state v with respect to the one of the state i. Here, we consider two identical photons and use single mode excitations of the radiation field with energy $\hbar\omega$, wave vector $\vec{k}$, and unit polarization vector $\vec{\mathcal{E}}$. Equation (1) is derived in the framework of the dipolar approximation and $\vec{D}$ refers to the dipole moment operator for the eight electrons of the configuration $3d^8$ while $\vec{D}.\vec{\mathcal{E}}$ stands for the scalar product of $\vec{D}$ and $\vec{\mathcal{E}}$.

The sum on v in (1) can be handled by using a quasi-closure approximation.[1] As a result, $M_{i\rightarrow f}$ turns out to be the matrix element of an effective operator H_{eff} between the initial and final electronic state vectors.[1,3] Following the phenomenological argument of Ref. 8, the operator H_{eff} may be extended to the form

$$H_{eff} \;=\; \sum_{k_S k_L k} C\left[\left(k_S k_L\right)k\right]\;\left(\mathbf{W}^{(k_S k_L)k}\,.\,\{\mathcal{E}\mathcal{E}\}^{(k)}\right)\,. \tag{2}$$

The polarization dependence in Eq. (2) is given by the tensor product $\{\mathcal{E}\mathcal{E}\}^{(k)}$ where k can be only 0 and 2 for identical photons. The electronic dependence is contained in the double tensor $\mathbf{W}^{(k_S k_L)k}$ of spin rank k_S, orbital rank k_L, and total rank k. The electronic and polarization parts are coupled together through the scalar product (.) occuring in (2). The parameters $C\left[(k_S k_L)k\right]$ depend on the configuration $3d^8$ and on the $3d^7 n'\ell'$ and $n'\ell'^{4\ell'+1}3d^9$ configurations to which the intermediate state vectors belong (the most important excited configuration is probably $3d^7 4p$). These parameters are clearly model-dependent and may be calculated from first principles. For example, the parameter C[(02)2], which we shall use in Sec. IV, reads

$$C\left[(02)2\right] \;=\; -\,\sqrt{2}\,e^2\,\sum_{n'\ell'}\,\left[\hbar\omega - E(n'\ell')\right]^{-1}\;\left(3d|r|n'\ell'\right)^2\,\left(2\|C^{(1)}\|\ell'\right)^2\,\left\{\begin{array}{ccc}1 & 2 & 1\\ 2 & \ell' & 2\end{array}\right\}\,, \tag{3}$$

where $E(n'\ell')$ is an average energy arising from the quasi-closure approximation.

In Eq. (2), the contribution $(k_S = 0, k_L = 2, k = 2)$ described by (3) corresponds to the second-order mechanism first introduced by Axe.[1] The other contributions ($k_S \neq$

$0, k_L, k$) correspond to higher-order mechanisms ; in particular, the contribution ($k_S = 1, k_L = 1, k = 0$) may correspond to third-order mechanisms taking into account the spin-orbit interaction within the $3d^7 n'\ell'$ configurations. (Contributions of the type ($k_S \neq 0, k_L, k$) were originally introduced in Refs. 3 and 4 in the case of lanthanide ions.) Alternatively, the contributions ($k_S \neq 0, k_L, k$) can be considered as (minimal) phenomenological extensions of the contribution ($k_S = 0, k_L = 2, k = 2$).[8]

Let us now describe the state vectors to be used for calculating the matrix elements of H_{eff}. The initial state vectors can be developed as

$$|i\Gamma\gamma) \equiv |3d^8 i\Gamma\gamma) = \sum_{SLJ} |3d^8 SLJ\Gamma\gamma)\, c(SLJ\Gamma; i) \tag{4}$$

in terms of symmetry adapted state vectors

$$|3d^8 SLJ\Gamma\gamma) = \sum_{M=-J}^{J} |3d^8 SLJM)\, (JM|J\Gamma\gamma)\ , \tag{5}$$

where the reduction coefficients $(JM|J\Gamma\gamma)$ allow to pass from the chain $SO(3) \supset SO(2)$ ($\{JM\}$ scheme) to the chain $SO(3) \supset O$ ($\{J\Gamma\gamma\}$ scheme). The only good quantum numbers in Eq. (4) are Γ and γ, where $\Gamma \equiv \Gamma(O)$ stands for an irreducible representation class (IRC) of the octahedral group O and γ is a multiplicity label for distinguishing the various partner wave-functions associated to the same Γ. (The label γ is really necessary only when the dimension of Γ is greater than 1.) Similarly, we take the final state vectors in the form

$$|f\Gamma'\gamma') \equiv |3d^8 f\Gamma'\gamma') = \sum_{S'L'J'} |3d^8 S'L'J'\Gamma'\gamma')\, c(S'L'J'\Gamma'; f)\ . \tag{6}$$

The c parameters in (4) and (6) may be obtained by diagonalizing, within the configuration $3d^8$, some Hamiltonian describing the Coulomb, spin-orbit, and crystal-field interactions. When dealing with Eq. (9) below, it is important to note that the parameters $c(SLJ\Gamma; i)$ and $c(S'L'J'\Gamma'; f)$ can be chosen in such a way that they do not depend on γ (for Γ fixed) and γ' (for Γ' fixed), respectively.

The matrix element $M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')}$ of the operator H_{eff} between the state vectors (4) and (6) may be calculated by using the Wigner-Racah algebra for the chain of groups $SO(3) \supset O$. Such a calculation has been done in Ref. 8 for a general configuration $n\ell^N$ in an arbitrary symmetry G. As a result, by taking $G \equiv O$ and $n\ell^N \equiv 3d^8$, we obtain

$$\begin{aligned} M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')} \;=\; & \sum_{S'L'J'} \sum_{SLJ} c(S'L'J'\Gamma';f)^*\; c(SLJ\Gamma;i) \\ & \sum_{k_S k_L k} (-)^{k_S+k_L-k}\; C[(k_S k_L)k]\; (3d^8 SLJ\|W^{(k_S k_L)k}\|3d^8 S'L'J')^* \\ & \sum_{\Gamma''\gamma''} f\begin{pmatrix} J & J' & k \\ \Gamma\gamma & \Gamma'\gamma' & \Gamma''\gamma'' \end{pmatrix}^*\; \{\mathcal{E}\mathcal{E}\}^{(k)}_{\Gamma''\gamma''}\;, \end{aligned} \tag{7}$$

where

$$\begin{aligned} f\begin{pmatrix} J & J' & k \\ \Gamma\gamma & \Gamma'\gamma' & \Gamma''\gamma'' \end{pmatrix} \;=\; & \sum_{MqM'} (-)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \\ & (JM|J\Gamma\gamma)^*\; (kq|k\Gamma''\gamma'')\; (J'M'|J'\Gamma'\gamma') \end{aligned} \tag{8}$$

is a coupling coefficient adapted to the chain $SO(3) \supset O$.

The next step is to calculate the intensity strength

$$S_{\Gamma\to\Gamma'} \;=\; \sum_{\gamma\gamma'} \left|M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')}\right|^2\;. \tag{9}$$

The sum on γ and γ' in (9) can be handled by employing : (i) the factorization property[14] for the f coefficients and (ii) the so-called orthonormality-completeness property[15] for the Clebsch-Gordan coefficients of the group O. This leads to the final result

$$S_{\Gamma\to\Gamma'} \;=\; \sum_{k=0,2} \sum_{\ell=0,2} \sum_{\Gamma''} \chi[k\Gamma'';\Gamma\Gamma']\; \chi[\ell\Gamma'';\Gamma\Gamma']^* \sum_{\gamma''} \{\mathcal{E}\mathcal{E}\}^{(k)}_{\Gamma''\gamma''}\; \left(\{\mathcal{E}\mathcal{E}\}^{(\ell)}_{\Gamma''\gamma''}\right)^*\;, \tag{10}$$

which is a particular case of the general result reported in Ref. 11 for a configuration $n\ell^N$ in symmetry G. The χ coefficients in (10) are given by

$$\begin{aligned} \chi[K\Gamma'';\Gamma\Gamma'] \;=\; & [\Gamma'']^{-1/2}\; [\Gamma]^{1/2} \sum_{S'L'J'} \sum_{SLJ} [J]^{-1/2} \\ & c(S'L'J'\Gamma';f)^*\; c(SLJ\Gamma;i) \sum_{k_S k_L} C[(k_S k_L)K] \\ & (-)^{k_S+k_L-K}\; (3d^8 SLJ\|W^{(k_S k_L)K}\|3d^8 S'L'J')^*\; (J'\Gamma' + K\Gamma''|J\Gamma) \end{aligned} \tag{11}$$

with $K = k, \ell$. In Eq. (11), the coefficient $(\ + \ | \ )$ stands for an isoscalar factor[14,16] for the chain $SO(3) \supset O$. Equations (10) and (11) take into account the fact that the octahedral group O is a multiplicity-free group (so that no internal multiplicity label β is necessary in (10) and (11)).

The polarization dependence in Eq. (10) is decribed by the symmetry adapted factors $\{\mathcal{E}\mathcal{E}\}^{(K)}_{\Gamma''\gamma''}$ (with $K = k, \ell$) defined by

$$\{\mathcal{E}\mathcal{E}\}^{(K)}_{\Gamma''\gamma''} \ = \ \sum_{Q=-K}^{K} \{\mathcal{E}\mathcal{E}\}^{(K)}_{Q} \ (KQ|K\Gamma''\gamma'') \tag{12}$$

in terms of the coupled spherical components

$$\{\mathcal{E}\mathcal{E}\}^{(K)}_{Q} \ = \ (-)^{K-Q} \ [K]^{1/2} \ \sum_{x \, y} \begin{pmatrix} 1 & K & 1 \\ x & -Q & y \end{pmatrix} \ (\mathcal{E})_x \ (\mathcal{E})_y \ , \tag{13}$$

where the spherical components $(\mathcal{E})_q$ (with $q = -1, 0, +1$) of the polarization vector $\mathcal{E} \equiv \mathcal{E}^{(1)}$ are given by

$$(\mathcal{E})_0 \ = \ \cos\Phi \ , \qquad\qquad (\mathcal{E})_{\pm 1} \ = \ \mp \frac{1}{\sqrt{2}} \ \sin\Phi \ e^{\pm i\theta} \tag{14}$$

for linear polarization and by

$$\big((\mathcal{E})_{-1}, (\mathcal{E})_0, (\mathcal{E})_{+1}\big) \ = \ (0, 0, -1) \quad \text{or} \quad (-1, 0, 0) \tag{15}$$

for circular polarization. We shall continue to develop the formalism for a general polarization although the experimental results in Ref. 13 are concerned only with a linear polarization for which the polar angles (Φ, θ) are $\Phi = \pi/2$ and $\theta = 0$ or $\pi/4$; this will enable us to make some theoretical predictions in Sec. V.

The number of independent χ parameters in (10) is controlled by the two following rules. First, we have a group-theoretical rule indicating that the sum over Γ'' in Eq. (10) is limited by

$$\Gamma'' \subset (k) \ , \qquad\qquad \Gamma'' \subset (\ell) \ , \qquad\qquad \Gamma'' \subset \Gamma'^{*} \otimes \Gamma \ , \tag{16}$$

where (k) and (ℓ) refer to IRC's of the group $SO(3)$ and $\Gamma'^{*}\otimes\Gamma$ is the Kronecker product of $\Gamma'^{*} \equiv \Gamma'$ and Γ. Therefore, the possible Γ'' in (10) are determined once the range of values for k and ℓ as well as the symmetries Γ and Γ' of the initial and final states are known. Second, the range of values for k and ℓ is partly fixed by the following model-dependent rule. For identical photons, we have : (i) either $k, \ell = 2$ for second-order mechanism (corresponding to $k_S = 0$) or (ii) $k, \ell = 0$ and 2 for second- plus third-order mechanisms (corresponding to $k_S = 0$ plus $k_S \neq 0$). The two preceeding rules, used in conjunction with a model for determining the initial and final state vectors, allow us to restrict the sums on k, ℓ, and Γ'' in the basic intensity formula (1), as we shall see in Secs. III and IV.

III. APPLICATION

We now apply the formalism described in Sec. II to the case where $i = {}^3A_2(T_2)$ for the initial state and $f = {}^3T_2(A_2, E, T_1, T_2)$, ${}^1E(E)$, ${}^3T_1(A_1, E, T_1, T_2)$, ${}^1T_2(T_2)$, and ${}^1A_1(A_1)$ for the final states. We thus have $\Gamma = T_2$ and $\Gamma' = A_1, A_2, E, T_1, T_2$. Since $(0) = A_1$ and $(2) = E \oplus T_2$ in terms of IRC's of O, Eq. (10) can be simplified to give

$$S_{\Gamma\to\Gamma'} \;=\; |\chi[0A_1;\Gamma\Gamma']|^2 \left|\{\mathcal{E}\mathcal{E}\}^{(0)}_{A_1}\right|^2 \;+\; \sum_{\Gamma''} |\chi[2\Gamma'';\Gamma\Gamma']|^2 \sum_{\gamma''} \left|\{\mathcal{E}\mathcal{E}\}^{(2)}_{\Gamma''\gamma''}\right|^2 , \qquad (17)$$

where the sum over Γ'' is limited to those IRC's E and T_2 occuring in $\Gamma' \otimes \Gamma$.

At this stage, the indices of type γ (like γ'' in Eq. (17)) can be taken in the form $\gamma \equiv \Gamma(D_4)\Gamma(D_2)$, where $\Gamma(D_4)$ and $\Gamma(D_2)$ denote IRC's of the subgroups D_4 and D_2 of O, respectively. Then, the polarization dependence in Eq. (17) is easily calculated using the chain $SO(3) \supset O \supset D_4 \supset D_2$ with the reduction coefficients $(JM|J\Gamma\gamma)$ defined

via[15]

$$
\begin{aligned}
|0A_1A_1A) &= |00) \ , \\
|2EA_1A) &= |20) \ , \\
|2EB_1A) &= \frac{1}{\sqrt{2}} \left[|22) \ + \ |2-2)\right] \ , \\
|2T_2B_2B_1) &= \frac{1}{\sqrt{2}} \left[|22) \ - \ |2-2)\right] \ , \\
|2T_2EB_2) &= \frac{i}{\sqrt{2}} \left[|21) \ - \ |2-1)\right] \ , \\
|2T_2EB_3) &= \frac{-1}{\sqrt{2}} \left[|21) \ + \ |2-1)\right]
\end{aligned}
\tag{18}
$$

in terms of symmetry adapted state vectors of type $|J\,\Gamma(O)\,\Gamma(D_4)\,\Gamma(D_2))$.

From Eqs. (12), (13), and (18), we get

$$
\begin{aligned}
\{\mathcal{E}\mathcal{E}\}^{(0)}_{A_1A_1A} &= \frac{-1}{\sqrt{3}} \qquad \text{or} \qquad 0 \ , \\
\{\mathcal{E}\mathcal{E}\}^{(2)}_{EA_1A} &= \frac{1}{\sqrt{6}} \left(3\cos^2\Phi - 1\right) \qquad \text{or} \qquad 0 \ , \\
\{\mathcal{E}\mathcal{E}\}^{(2)}_{EB_1A} &= \frac{1}{\sqrt{2}} \ \sin^2\Phi \ \cos 2\theta \qquad \text{or} \qquad \frac{1}{\sqrt{2}} \ , \\
\{\mathcal{E}\mathcal{E}\}^{(2)}_{T_2B_2B_1} &= \frac{i}{\sqrt{2}} \ \sin^2\Phi \ \sin 2\theta \qquad \text{or} \qquad \pm\frac{1}{\sqrt{2}} \ , \\
\{\mathcal{E}\mathcal{E}\}^{(2)}_{T_2EB_2} &= \frac{-i}{\sqrt{2}} \ \sin 2\Phi \ \cos\theta \qquad \text{or} \qquad 0 \ , \\
\{\mathcal{E}\mathcal{E}\}^{(2)}_{T_2EB_3} &= \frac{i}{\sqrt{2}} \ \sin 2\Phi \ \sin\theta \qquad \text{or} \qquad 0
\end{aligned}
\tag{19}
$$

for linear or circular polarization, respectively. Thus, the possible polarization factors in Eq. (17) are

$$
\begin{aligned}
a &= \left|\{\mathcal{E}\mathcal{E}\}^{(0)}_{A_1}\right|^2 = \frac{1}{3} \qquad \text{or} \qquad 0 \ , \\
b &= \sum_{\gamma''} \left|\{\mathcal{E}\mathcal{E}\}^{(2)}_{E\gamma''}\right|^2 = \frac{1}{6} \left[(3\cos^2\Phi - 1)^2 + 3\sin^4\Phi \ \cos^2 2\theta\right] \qquad \text{or} \qquad \frac{1}{2} \ , \\
c &= \sum_{\gamma''} \left|\{\mathcal{E}\mathcal{E}\}^{(2)}_{T_2\gamma''}\right|^2 = \frac{1}{2} \left(\sin^4\Phi \ \sin^2 2\theta + \sin^2 2\Phi\right) \qquad \text{or} \qquad \frac{1}{2} \ .
\end{aligned}
\tag{20}
$$

Therefore, Eq. (17) can be expressed as

$$
S_{T_2\to\Gamma'} = a \ \left|\chi[0A_1; T_2\Gamma']\right|^2 + b \ \left|\chi[2E; T_2\Gamma']\right|^2 + c \ \left|\chi[2T_2; T_2\Gamma']\right|^2 \ , \tag{21}
$$

where $\Gamma' = A_1, A_2, E, T_1, T_2$. It should be emphasized that the χ parameters in Eq. (21) depend not only on the symmetry (i.e., Γ') of the involved final state but also on the corresponding electronic state vectors (cf., Eq. (6)).

The experimental situation described in Ref. 13 corresponds to the wave number $\vec{k}$ along one cube axis so that $\Phi = \pi/2$. Therefore, we have

$$\begin{aligned} b &= \frac{1}{2}\,(\cos^2 2\theta \,+\, \frac{1}{3}) \quad \text{or} \quad \frac{1}{2}\,, \\ c &= \frac{1}{2}\,\sin^2 2\theta \quad \text{or} \quad \frac{1}{2} \end{aligned} \tag{22}$$

and the θ-dependent intensities $S_{T_2 \to \Gamma'}$ with $\Gamma' = A_2, T_2, T_1, E, A_1$ are

$$\begin{aligned} S_{T_2 \to A_2} &= 0 \qquad \text{or} \qquad 0\,, \\ S_{T_2 \to T_2} &= \frac{1}{3}\,r^2 \,+\, \frac{1}{6}\,s^2\,(1 \,+\, 3\cos^2 2\theta) \,+\, \frac{1}{2}\,t^2\,\sin^2 2\theta \qquad \text{or} \qquad \frac{1}{2}\,(s^2 \,+\, t^2)\,, \\ S_{T_2 \to T_1} &= \frac{1}{6}\,u^2\,(1 \,+\, 3\cos^2 2\theta) \,+\, \frac{1}{2}\,v^2\,\sin^2 2\theta \qquad \text{or} \qquad \frac{1}{2}\,(u^2 \,+\, v^2)\,, \\ S_{T_2 \to E} &= \frac{1}{2}\,w^2\,\sin^2 2\theta \qquad \text{or} \qquad \frac{1}{2}\,w^2\,, \\ S_{T_2 \to A_1} &= \frac{1}{2}\,x^2\,\sin^2 2\theta \qquad \text{or} \qquad \frac{1}{2}\,x^2 \end{aligned} \tag{23}$$

for linear or circular polarization, respectively. In Eq. (23), we have introduced the non-negative parameters

$$\begin{aligned} r^2 &= |\chi[0A_1; T_2T_2]|^2\,, \\ s^2 &= |\chi[2E; T_2T_2]|^2\,, \\ t^2 &= |\chi[2T_2; T_2T_2]|^2\,, \\ u^2 &= |\chi[2E; T_2T_1]|^2\,, \\ v^2 &= |\chi[2T_2; T_2T_1]|^2\,, \\ w^2 &= |\chi[2T_2; T_2E]|^2\,, \\ x^2 &= |\chi[2T_2; T_2A_1]|^2\,. \end{aligned} \tag{24}$$

It should be observed that $r = 0$ if we restrict ourselves to second-order mechanisms.

Equation (23) gives the detailed polarization dependence of the intensity for the various two-photon transitions. For linear polarization, Eq. (23) can be particularized to the special case $\theta = 0$ and $\theta = \pi/4$ corresponding to the experimental results reported in Ref. 13 (light polarized along the (100) and (110) axes, respectively). Then, the ratios considered in Ref. 13 for the transitions ${}^3A_2(T_2) \rightarrow {}^3T_2(E, T_1)$ assume the form

$$\begin{aligned} R_1 &= \frac{S_{T_2\rightarrow T_1}(\theta = 45^\circ)}{S_{T_2\rightarrow T_1}(\theta = 0^\circ)} = \frac{1}{4}\,\left(1 + 3\,\frac{v^2}{u^2}\right)\ , \\ R_2 &= \frac{S_{T_2\rightarrow T_1}(\theta = 45^\circ)}{S_{T_2\rightarrow E}(\theta = 45^\circ)} = \frac{1}{3}\,\frac{u^2 + 3\,v^2}{w^2} \end{aligned} \tag{25}$$

and will serve for testing our theory. We shall also consider ratios, similar to R_1, defined for any final state of symmetry $\Gamma' = A_1, A_2, E, T_1, T_2$ by

$$R = \frac{S_{T_2\rightarrow \Gamma'}(\theta = 45^\circ)}{S_{T_2\rightarrow \Gamma'}(\theta = 0^\circ)}\ , \tag{26}$$

where, according to Eqs. (21) and (22), we have

$$\begin{aligned} S_{T_2\rightarrow \Gamma'}(\theta = 45^\circ) \ &= \ \frac{1}{3}\ \left|\chi[0A_1; T_2\Gamma']\right|^2 \ + \ \frac{1}{6}\ \left|\chi[2E; T_2\Gamma']\right|^2 \ + \ \frac{1}{2}\ \left|\chi[2T_2; T_2\Gamma']\right|^2\ , \\ S_{T_2\rightarrow \Gamma'}(\theta = 0^\circ) \ &= \ \frac{1}{3}\ \left|\chi[0A_1; T_2\Gamma']\right|^2 \ + \ \frac{2}{3}\ \left|\chi[2E; T_2\Gamma']\right|^2\ . \end{aligned} \tag{27}$$

Note that in the case where $f = {}^3T_2(\Gamma' = T_1)$, R is nothing but R_1.

IV. RESULT

The intensity parameters $\chi[k\Gamma''; T_2\Gamma']$ in Eq. (24) can be obtained with the help of the definition (11). The expansion coefficients $c(SLJ\Gamma; i)$ and $c(S'L'J'\Gamma'; f)$ in Eq. (11) can be derived by diagonalizing the appropriate Hamiltonian within the configuration $3d^8$. Such a diagonalization has been done by Campochiaro *et al.*[13] who used the simple model developed by Liehr and Ballhausen.[17] However, the wave-functions in

Ref. 13 are given in the strong-field basis and, in order to get the c coefficients, they have to be transformed to the weak-field basis. This can be achieved by means of the transformation matrices set up in Ref. 17. As a result, the wave-functions corresponding to the sixteen strong-field states considered in Ref. 13 are described in Table I in a weak-field basis.

Looking at Table I, we note that in most cases the dominating weak-field components of the initial state ${}^3A_2(T_2)$ can be connected to the dominating weak-field components of the final state via the tensor operator $\mathbf{W}^{(02)2}$ arising in the standard second-order model of intra-configurational two-photon absorption. This is an indication that the second-order mechanism depicted by $C[(02)2]$ in Eq. (11) should be sufficient to interpret the two-photon transitions in the case of Ni^{2+} in MgO. We may then limit our analysis to the contribution $(k_S = 0, k_L = 2, k = 2)$. The only free parameter is then $C[(02)2]$. It can be calculated from

$$C[(02)2] \;=\; -\frac{1}{5}\,\sqrt{\frac{14}{3}}\;e^2\;\frac{\left(3d|r|4p\right)^2}{[\hbar\omega - E(4p)]} \tag{28}$$

which follows from Eq. (3) provided we restrict the sum over $n'\ell'$ to $n'\ell' \equiv 4p$. The magnitude of the parameter $C[(02)2]$ can be estimated by taking the reasonable value $E(4p) \approx (3/4)R_\infty$ (R_∞ = Rydberg constant) and by using the radial integrals tabulated in Ref. 18. However, this magnitude is the same for all the transitions to be considered, so we can normalize it to any convenient value. For our calculations we take $C[(02)2] = 4\,\sqrt{\frac{35}{3}}$.

The reduced matrix elements in Eq. (11) follow from the tables in Ref. 19 owing to $\mathbf{W}^{(02)2} = \sqrt{\frac{5}{2}}\;\mathbf{U}^2$. The isoscalar factors $(J'\Gamma' + K\Gamma''|J\Gamma)$ in (11) can be calculated by applying the method developed in Ref. 14 to the data of Ref. 15 ; alternatively, they can

be deduced from the $SO(3) \supset O$ factors of Ref. 20 by means of the connecting formula

$$(J'\Gamma' + K\Gamma''|J\Gamma) \;=\; \sqrt{\frac{[J]}{[\Gamma]}} \begin{pmatrix} J & K & J' \\ \Gamma & \Gamma'' & \Gamma' \end{pmatrix}^{SO(3)}_{O} \tag{29}$$

which arises by expressing, in the notations of Refs. 15 and 20, the Wigner-Eckart theorem for the groups $SO(3)$ and O in an $SO(3) \supset O$ basis.

By following the scheme just described, we finally obtain the values of the χ parameters, the intensity parameters (23), and the intensities (27). These intensities together with the ratio R are presented in Table II.

V. CONCLUSION

We have concentrated in this paper on a model for describing two-photon intraconfigurational transitions for an ion with d^8 or d^2 configuration in a surrounding of octahedral symmetry. The model is based on the consideration of second-order mechanisms with ionic wave-functions as the initial and final state vectors. Furthermore, the information on symmetry manifests itself in this model through the quantitative use of symmetry adaptation techniques for the chain of groups $SO(3) \supset O$. The model leads to intensity formulas in the spirit of those derived in Refs. 8, 9, and 11 for a configuration $n\ell^N$ in an arbitrary symmetry. These formulas exhibit the polarization dependence for linearly and circularly polarized photons in terms of intensity parameters which depend on a single parameter (viz., $C[(02)2]$).

In the case of linearly polarized photons, the application of the latter formulas to Ni^{2+} in MgO yields theoretical intensities in reasonable agreement with the experimental values of Ref. 13. There is no experimental result for circularly polarized photons, so that our results provide predictions in this case.

Our results concern the two-photon transitions from the ground state $^3A_2(T_2)$ to

the first fifteen excited states of MgO:Ni^{2+}. The polarization ratios R_1 and R_2 defined by Eq. (25) for the transitions ${}^3A_2(T_2) \rightarrow {}^3T_2(E, T_1)$ are of special interest for testing purposes because of the particularly good resolution of these transitions. The reported experimental values of R_1 and R_2 are 3.0 and 1.1, respectively. From Table II, we can obtain the theoretical values of R_1 and R_2 : we find $R_1 \equiv R = 0.95$ and we calculate, using Eq. (25), $R_2 = 1.04$. Note that the theoretical values obtained in Ref. 13 are $R_1 = 220$ and $R_2 = 25$. To get the experimental values of R_1 and R_2, the parameters u^2, v^2, and w^2 occurring in Eq. (23) would have to satisfy the relations $u^2/w^2 = 0.28$ and $v^2/w^2 = 1$. The introduction of the latter relations into Eq. (23) may give predictions on the polarization dependence of the transitions ${}^3A_2(T_2) \rightarrow {}^3T_2(E, T_1)$ for any value of θ in term of a single parameter (say, w^2).

Is it possible to improve the model ? As can be easily proved, the third-order (spin-orbit) correction[3,4] has in our case very limited significance. First, its leading term is proportional to the tensor operator $\mathbf{W}^{(11)0}$ and gives a vanishing contribution since this operator cannot link ${}^3A_2(T_2)$ and ${}^3T_2(E, T_1)$. Second, the reamaining terms (arising from the tensors $\mathbf{W}^{(1k_L)2}$) give, according to an aside calculation, corrections of an order of a few percents.

Another possible improvement of the model might come, as already mentioned by McClure and co-workers,[13] from dynamic contributions of the ligands. In this respect, however, much more extensive and involved studies are needed to reach conclusions.

To close, it is worth noticing that the approach presented in Secs. II and III can be extended to any other transition-metal ion or any rare-earth ion in an arbitrary symmetry, possibly with two different photons (see Ref. 11 for further details). We also mention that a similar formalism can be developed for inter-configurational two-photon transitions.[21]

TABLE I. The wave-functions of the ion Ni^{2+} in MgO in a weak-field basis.

$$^3A_2(T_2) = 0.02\ i\ |^1G_4) + 0.02\ i\ |^1D_2) - 0.55\ |^3F_3) + 0.72\ i\ |^3F_4) - 0.41\ i\ |^3F_2)$$

$$^3T_2(E) = -0.03\ |^3P_2) - 0.475\ |^3F_2) - 0.87\ |^3F_4)$$
$$^3T_2(T_1) = -0.03\ |^3P_1) - 0.72\ |^3F_3) + 0.69\ i\ |^3F_4)$$
$$^3T_2(T_2) = 0.03\ i\ |^3P_2) + 0.31\ |^3F_3) + 0.64\ i\ |^3F_4) + 0.70\ i\ |^3F_2)$$
$$^3T_2(A_2) = -i\ |^3F_3)$$

$$^1E(E) = -0.44\ |^1G_4) + 0.73\ |^1D_2) + 0.25\ |^3P_2) - 0.36\ |^3F_2) + 0.27\ |^3F_4)$$

$$a\ ^3T_1(A_1) = 0.34\ i\ |^3P_0) - 0.94\ i\ |^3F_4)$$
$$a\ ^3T_1(T_1) = -0.35\ |^3P_1) + 0.65\ |^3F_3) + 0.66\ i\ |^3F_4)$$
$$a\ ^3T_1(T_2) = -0.39\ i\ |^3P_2) + 0.73\ |^3F_3) + 0.28\ i\ |^3F_4) - 0.49\ i\ |^3F_2)$$
$$a\ ^3T_1(E) = 0.33\ |^1G_4) - 0.38\ |^1D_2) + 0.33\ |^3P_2) - 0.73\ |^3F_2) + 0.32\ |^3F_4)$$

$$^1T_2(T_2) = 0.38\ i\ |^1G_4) + 0.82\ i\ |^1D_2) + 0.39\ i\ |^3P_2) + 0.11\ |^3F_3)$$
$$+ 0.04\ i\ |^3F_4) - 0.07\ i\ |^3F_2)$$

$$^1A_1(A_1) = 0.25\ i\ |^1S_0) + 0.95\ i\ |^1G_4) - 0.05\ i\ |^3P_0) - 0.10\ i\ |^3F_4)$$

$$b\ ^3T_1(E) = -0.91\ |^3P_2) - 0.33\ |^3F_2) + 0.24\ |^3F_4)$$
$$b\ ^3T_1(T_2) = 0.28\ i\ |^1G_4) + 0.32\ i\ |^1D_2) - 0.83\ i\ |^3P_2) - 0.28\ |^3F_3)$$
$$- 0.11\ i\ |^3F_4) + 0.19\ i\ |^3F_2)$$
$$b\ ^3T_1(T_1) = 0.94\ |^3P_1) + 0.21\ |^3F_3) + 0.28\ i\ |^3F_4)$$
$$b\ ^3T_1(A_1) = -0.94\ i\ |^3P_0) - 0.34\ i\ |^3F_4)$$

TABLE II. The results of two-photon intensity calculations. The intensities S and the ratio R are defined by Eqs. (26) and (27). To get the intensities defined by (9), each S has to be multiplied by $(3/35)\ \{C[(02)2]/4\}^2$.

Strong-field term	Substate symmetry (Γ')	Intensity $S_{T_2\to\Gamma'}(0^\circ)$	Intensity $S_{T_2\to\Gamma'}(45^\circ)$	R
$^3T_2$	E	0	1.02	–
	T_1	1.11	1.06	0.95
	T_2	1.27	0.43	0.34
	A_2	0	0	–
^1E	E	0	0.35	–
$a\ ^3T_1$	A_1	0	0.44	–
	T_1	3.51	0.90	0.26
	T_2	0.92	7.30	7.93
	E	0	0.93	–
$^1T_2$	T_2	1.28	1.68	1.31
$^1A_1$	A_1	0	0.01	–
$b\ ^3T_1$	E	0	3.24	–
	T_2	5.88	7.18	1.22
	T_1	5.51	7.50	1.36
	A_1	0	0.06	–

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